

Net ecosystem exchange of carbon dioxide in a temperate poor fen: a comparison of automated and manual chamber techniques

ELIZABETH H. BURROWS^{1,2,*}, JILL L. BUBIER¹, ANDREW MOSEDALE⁴, GEORGE W. COBB⁴ and PATRICK M. CRILL^{3,5}

¹Environmental Studies Program, Department of Earth and Environment, Mount Holyoke College, 50 College Street, South Hadley, MA 01075, USA; ²Department of Bioresource Engineering, Oregon State University, 116 Gilmore Hall, Corvallis, OR 97331, USA; ³Complex Systems Research Center, Institute for the Study of Earth, Oceans and Space, University of New Hampshire, Durham, NH 03824, USA; ⁴Department of Mathematics and Statistics, Mount Holyoke College, 50 College Street, South Hadley, MA 01075, USA; ⁵Department of Geology and Geochemistry, University of Stockholm, 106 91 Stockholm, Sweden; *Author for correspondence: Department of Bioresource Engineering, Oregon State University, 116 Gilmore Hall, Corvallis, OR 97331, USA (e-mail: burrowse@engr.orst.edu; phone: +1-541-754-1048)

Received 30 July 2004; accepted in revised form 16 November 2004

Key words: Automated chambers, Chamber comparison, CO₂ flux, Fen, Net ecosystem CO₂ exchange, Wetland

Abstract. We used five analytical approaches to compare net ecosystem exchange (NEE) of carbon dioxide (CO₂) from automated and manual static chambers in a peatland, and found the methods comparable. Once per week we sampled manually from 10 collars with a closed chamber system using a LiCor 6200 portable photosynthesis system, and simulated four photosynthetically active radiation (PAR) levels using shrouds. Ten automated chambers sampled CO₂ flux every 3 h with a LiCor 6252 infrared gas analyzer. Results of the five comparisons showed (1) NEE measurements made from May to August, 2001 by the manual and automated chambers had similar ranges: -10.8 to $12.7 \mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$ and -17.2 to $13.1 \mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$, respectively. (2) When sorted into four PAR regimes and adjusted for temperature (respiration was measured under different temperature regimes), mean NEE did not differ significantly between the chambers ($p < 0.05$). (3) Chambers were not significantly different in regression of $\ln(-\text{respiration})$ on temperature. (4) But differences were found in the PAR vs. NEE relationship with manual chambers providing higher maximum gross photosynthesis estimates (GP_{max}), and slower uptake of CO₂ at low PAR (α) even after temperature adjustment. (5) Due to the high variability in chamber characteristics, we developed an equation that includes foliar biomass, water table, temperature, and PAR, to more directly compare automated and manual NEE. Comparing fitted parameters did not identify new differences between the chambers. These complementary chamber techniques offer a unique opportunity to assess the variability and uncertainty in CO₂ flux measurements.

Introduction

As evidence mounts that the climate is becoming warmer and drier in the northern mid-latitudes (Gregory et al. 1997; De Villiers 2000), it becomes ever more crucial to accurately quantify the processes that control sources and sinks of CO₂, a leading greenhouse gas. Peatlands have historically been a net sink of

carbon due to their water-logged, anaerobic soils where decomposition is slow compared to upland systems, and the associated vegetation is decay-resistant (Hobbie 1996; Frohling et al. 1998). But their ability to store carbon in the future is uncertain. Warmer, drier weather could cause the water level in northern Canadian fens to decrease by a predicted 14 cm (Waddington et al. 1998), releasing much of the stored biomass carbon. The soils would become aerobic, giving microbes the oxygen they need to more efficiently decompose the accumulated biomass. Peatlands therefore could be converted from a sink to a source of CO₂ (Oechel 1993; Brown 1998; Alm et al. 1999; Bubier et al. 1999; Joiner et al. 1999; Aurela et al. 2001). Shurpali et al. (1995) sampled CO₂ flux in a peatland during two consecutive years, and found the peatland was a net sink of CO₂ during the cooler, wetter year, and a net source of CO₂ during the warmer, drier year. Alternatively, Bubier et al. (2003b), Waddington et al. (1998), and Laine and Minkkinen (1996) found that for northern peatlands that are already excessively wet, water table lowering would promote greater carbon storage, depending on plant species composition, nutrient status, and tree cover. Because the CO₂ source–sink strength of peatlands can vary spatially and on short time-scales, it is important to make accurate measurements of net ecosystem CO₂ exchange and understand the magnitude and sources of measurement uncertainty.

Carbon dioxide flux is quantified using several different approaches. The techniques in use include micrometeorological methods such as eddy covariance (Vourlitis and Oechel 1999; Barford et al. 2001; Lafleur et al. 2001, 2003), aircraft measurements, CO₂ concentration gradients in large bodies of water and direct measurements using various types of chambers. Chamber types include static, air-tight chambers and dynamic, flow-through chambers. Methods of measurement involving closed chambers that follow CO₂ mixing ratio changes in an isolated headspace above the surface (e.g. Conen and Smith 2000) are perhaps the most common techniques for quantifying peatland CO₂ exchange. Chambers can be operated manually or be programmed to make measurements automatically. Each approach has advantages. Automated chambers allow high temporal sampling frequency from limited areas whereas manual chambers allow low density sampling over broad sample areas. Here we report on a comparison of fluxes determined in the same small wetland with automated static chambers (e.g. Goulden and Crill 1997) and fluxes made using a common portable manual static chamber technique (e.g. Whiting et al. 1991; Bubier et al. 1998). Manual chambers require greater time and physical labor, and logistics make it more difficult to obtain nighttime and winter measurements. Drawbacks to the automated chambers include their spatial restriction, high cost and power requirement. Given the numerous methods for calculating, measuring, and modeling CO₂ flux, it is important to determine their reliability, precision, accuracy (Ambus and Robertson 1998; Bubier et al. 1999; Pumpanen et al. 2001; Davidson et al. 2002; King and Harrison 2002) and, perhaps most importantly, their comparability.

Sallie's Fen is unique in that both automated and manual chambers have been operational since June, 2000 when the automated system was installed. The purpose of this study was to compare NEE measured by each chamber type, taking into account factors such as temperature, PAR, plant biomass, and water table. Examining how automated and manual chamber NEE differs in response to these factors will help determine which system is preferable for answering various ecological questions. Accounting for other chamber characteristics will isolate the effect of chamber type on NEE.

Materials and methods

Site description

Sallie's Fen is a minerotrophic poor fen in Barrington, New Hampshire, USA (43°12.5' N, 71°3.5' W). This study focused on data collected during the 2001 growing season, the first complete growing season for which the automated system was functioning. Surface water pH ranged from 3.2 to 5.9 during the 2001 field season. In July, 2001 surface peat ranged from 5 to 35 cm above water table, and aboveground vascular plant biomass ranged from 100 to 1000 g m⁻². CO₂ and CH₄ gas flux data have been collected manually from this 1.7-ha peatland since 1989 (e.g. Froelking and Crill 1994; Melloh and Crill 1996; Carroll and Crill 1997). During the relatively warm, dry growing season of 1994, the fen lost approximately 145 g C m⁻² (Carroll and Crill 1997). Comparing wet vs. dry summers of 2000 and 2001, shrubs had higher net CO₂ uptake under dry conditions than sedges (Bubier et al. 2003b).

There were 20 predominant plant species in the study plots, consisting of shrubs and sedges, with an under-story of *Sphagnum* mosses. Dominant species included leatherleaf (*Chamaedaphne calyculata* (L.) Moench), Carex sedge (*Carex rostrata* Stokes), small cranberry (*Vaccinium oxycoccus* (L.)), speckled alder (*Alnus incana* (L.) Moench), and *Sphagnum* mosses (*Sphagnum magellanicum* Brid. and *Sphagnum fallax* (Klinggr.) Klinggr.). The vegetation varied within the fen due to the presence of hummocks and hollows, nutrient and hydrologic gradients, and a lag, which ran along the northeast edge of the fen (Carroll and Crill 1997).

Chamber designs

Because we were comparing methodologies, we used our standard field techniques rather than trying to match up measurement strategies. Ten 60 × 60 cm aluminum collars (labeled m1–m10) were installed in the fen between 1989 and 1992 for manual chamber measurements of CO₂ and CH₄ fluxes (described in Carroll and Crill 1997) (Figure 1). The aluminum collars were imbedded 10–15 cm into the peat surface and had a groove for chamber placement in

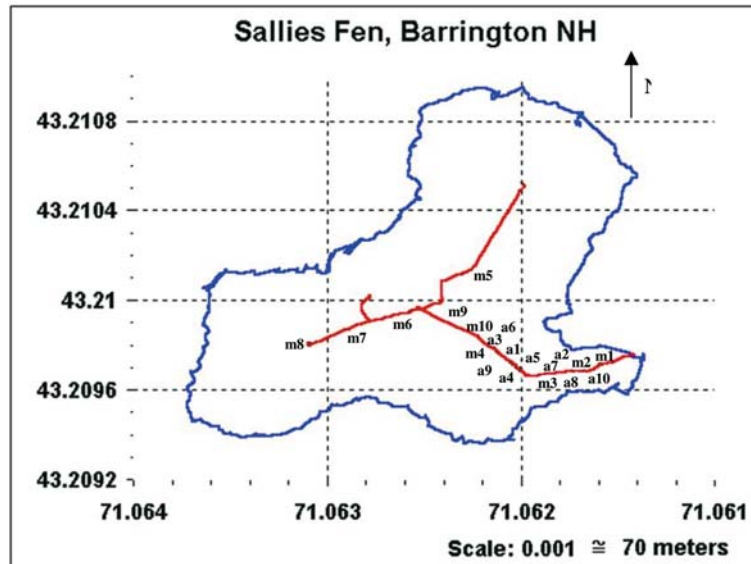


Figure 1. Map showing the location of the automated (ax) and manual (mx) chamber sites in Sallie's Fen (range from 71.061° to 71.064° N, and 43.2092° to 43.2108° W). Lines running through fen represent the boardwalk.

water to ensure an airtight seal. The manual chamber was 90.5 cm in height and was designed to move among collar locations. Three walls were made of 1.27 mm Teflon film; the fourth side and the removable lid were made with 3.2 mm Lexan for added support. An aluminum frame held the four walls and the lids together. The Teflon and Lexan used in the chambers reduced PAR less than 10% (Czepiel, unpublished data). The manual chamber had two 12 V brushless muffin fans for circulating the air within the chamber. For the manual chamber, during extremely hot days, a cooling system was used that circulated ice water through a heat exchanger attached to the chamber wall. Air was then circulated by fans inside the chamber to maintain headspace temperature to within 1 °C of ambient. The climate-control system also kept relative humidity at a more constant level to prevent condensation from forming on the chamber walls.

The automatic CO₂ exchange control and analysis system at Sallies Fen was similar in design to one used by Goulden and Crill (1997) at a black spruce forest in central Manitoba. The chamber design was based on those used at the Organization for Tropical Studies station at La Selva, Costa Rica (e.g. Crill et al. 2000), although the chambers in this study (labeled a1–a10) were transparent and taller to enclose the plant canopy (for more specific details of the system design and operation, please contact Ruth Varner, Complex Systems Research Center, University of New Hampshire, ruth.varner@unh.edu). Ten automated chambers were installed in the fen in the spring of 2000. The chambers were

45.7 × 45.7 cm at the base, made entirely with 3.2 mm Lexan, and either 68 or 34 cm tall depending on the height of the vegetation (described in Bubier et al. 2002, 2003b). The walls of the chambers were imbedded 10–15 cm into the peat surface. Because the bases isolated the vegetation in the chambers from horizontal advection, each chamber was equipped with a brushless muffin fan (NMB, Minebea Co. Ltd., Thailand) that ran continuously during the summer months with a flow of 708–1301 l min⁻¹, to ensure that the air within the chamber was well mixed. Since the automated chambers did not have a cooling system, we restricted our flux calculations to the first 3–6 min after chamber closure.

Gas analysis and data collection

Manual CO₂ data were collected using a LiCor 6200 portable photosynthesis system, which included a LI-6250 IRGA (LiCor Inc., Lincoln, NE), datalogger, and sensor head with thermocouples and a relative humidity sensor. The LiCor 6200 also collected data regarding PAR, vapor pressure, date, and time, and was attached to the chamber with approximately 1 m of 0.32 cm inner diameter Bev-a-line tubing. The flow rate of the LiCor 6200 was kept at approximately 1200 ml/min. Carbon dioxide and environmental data were processed and stored in the datalogger during sampling, and were downloaded manually to a computer as an ASCII text file at the end of each sampling day.

In the automated chamber headspace a LiCor 6252 IRGA (LiCor Inc., Lincoln, NE) was used to determine the CO₂ concentration. The air stream into the IRGA was kept at a constant flow rate of 5000 cm³ min⁻¹ by a 10,000 cm³ min⁻¹ mass flow controller (MKS Instruments, Andover, MA). There was no detectable difference between the enclosed headspace air pressure and that of ambient air. The control system and gas analyzer were kept in a weatherproof box along with low voltage power supplies, sampling pump and solenoids. A 20.3 stroke double acting pneumatic cylinder (Clippard Minimatic, Cincinnati, OH) activated the automated chamber lids, coupled with a 4-way solenoid bank and an air compressor (GAST Manufacturing Inc., Bridgman, MI). Each chamber was attached to the control box through 0.64 cm inner diameter high-density polyethylene tubing (Read Plastics, Rockville, MD) that ranged from 5 to 27 m in length. For the chambers furthest from the control box, it took approximately 9.5 s for the gas samples in the headspace to reach the IRGA. A SM4M storage module (Campbell Scientific, Logan, UT) stored the raw data collected at the CR10X and was downloaded to a computer approximately once per week.

Sampling

Each manual collar was sampled once a week, in varying order to minimize the temporal bias. The manual chamber was moved to each of the 10 collars, and

four 2.5-minute sampling runs were conducted, each at a different light level: one run at ambient light level; two runs conducted with cloth shrouds, blocking out half and three-quarters of the light to simulate low PAR; and one flux run with an opaque shroud used to obtain dark respiration values. Between each run the chamber lid was removed and the chamber was allowed to equilibrate until CO₂ returned to ambient levels. Samples were generally taken between 10:00 and 14:00 when PAR was maximal and temperatures were high.

The automated chambers collected data throughout the diurnal cycle every 3 h from each of the 10 chambers. For the first 8 min of a 15-min sampling run, the lids remained open to flush the sample lines with ambient air. The rotation continued so that each chamber was sampled eight times per day at the same times every day.

Flux calculation

The duration of each manual run was 2.5 min. The LI-6250 IRGA sampled every 10 s, and computed a flux every 30 s to produce five fluxes per run. To avoid an underestimate in flux due to varying vapor pressure, all the data were adjusted using equations published by Hooper et al. (2002) and the change in vapor pressure recorded by the LiCor 6200. The effect of this correction increased with increasing PAR, and added on average 2.4% to respiration, and 8.5% to NEE at PAR > 1000. The final flux was the mean of the five 30-s fluxes. The five means were scanned and outliers were removed. The most common reason for removal of a data point was the occurrence of an unusually high initial flux (less negative) during the zero PAR runs, possibly due to the time taken to place the opaque shroud over the chamber. A common protocol used in previous analysis of this type of data was to exclude the last one or two flux values on high light runs if it was believed that the vegetation in the chamber was under stress due to increased humidity and temperature; this protocol was not used in the analysis of these data because the automated chamber flux calculation did not employ an analogous protocol.

As with the manual chamber system, each automated chamber flux was determined using a 2.5-min time span, with means calculated at 30-s intervals. However, the CR10X (Campbell Scientific, Logan, UT) logged the CO₂ concentration every 3 s, as opposed to the 10-s sampling interval used by the LiCor 6200 and its internal datalogger. In contrast to the manual system, data filtering was done before a flux was calculated. To obtain one NEE flux value, a method of calculating slopes and R^2 values from the ppmv CO₂ vs. time data was employed. Slopes and respective R^2 values were calculated from four sets of points: the first five means; second through sixth means; third through seventh means; and fourth through eighth means. For runs in which the ppmv CO₂ increased over a run (CO₂ emission), the set with the highest R^2 was used to compute NEE flux, whereas for runs in which the ppmv CO₂ decreased over a run (CO₂ uptake), the set with the largest slope was used. The reason for the differing

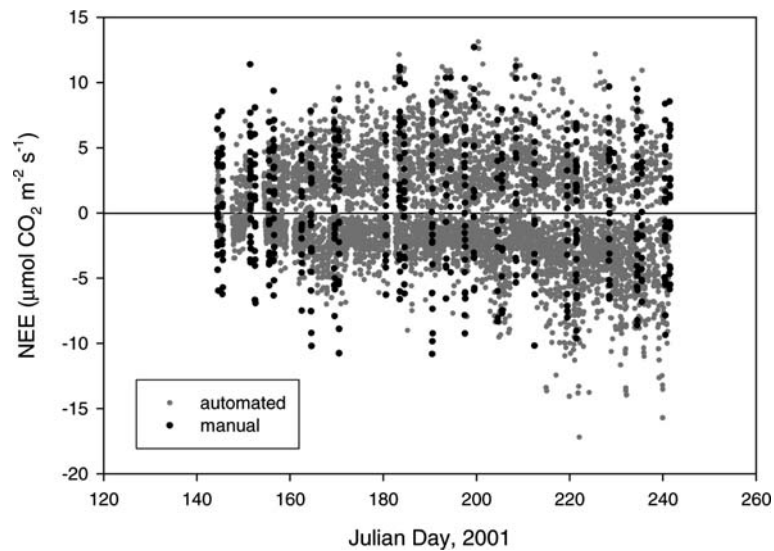


Figure 2. Overall seasonal pattern of NEE for the manual ($n = 530$) and automated ($n = 5126$) chambers from May 24 to August 29, 2001. Net uptake of CO_2 by the ecosystem is recorded as positive values while net release to the atmosphere is negative.

protocol was that when photosynthesis was greater than respiration (during high PAR and temperature), there was a risk that the plants would become stressed in the chamber and the rate of photosynthesis would decrease over time. Fluxes with $R^2 < 0.87$ were eliminated, constituting approximately 17% of the measured fluxes (Bubier et al. 2003b). The rejected fluxes were normally distributed around zero indicating no systematic bias. This method of filtering underestimated the contribution of near zero fluxes; 90% of the rejected fluxes were less than the minimal detectable flux of $0.09 \mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$ based on the chamber volume and analytical uncertainty (LiCor Inc., Lincoln, NE) of the IRGA system. We chose to focus on fluxes that had a high degree of analytical and statistical confidence (the decreased number of low fluxes is apparent in Figure 2). Although the automated protocol for flux calculation differed slightly from the manual protocol for logistical reasons, the most important aspects of the flux calculation were the same between the two systems.

Biomass estimates

In order to calculate vascular plant aboveground biomass, species composition was recorded in each collar on July 19, 2000 for all 10 manual collars and for all 10 automated chambers on July 19, 2001. Each vascular plant stem was counted and mean height from the peat surface was estimated. Also, during July 2000 six 60×60 cm plots (the size of the manual collars) were chosen at

Table 1. Linear equation statistics for the (biomass vs. stem number times mean height) relationships used to estimate plant biomass in the collars.

	Total/foliar biomass	Slope	<i>p</i> -value	<i>R</i> ²
Herbaceous plants	Total	0.0043	0.0000	0.84
	Foliar	0.0042	0.0000	0.89
Deciduous shrubs and trees	Total	0.3050	0.0449	0.46
	Foliar	0.1032	0.0015	0.78
Evergreen shrubs	Total	0.0192	0.0072	0.93
	Foliar	0.0108	0.0001	0.98
<i>Vaccinium oxycoccus</i>	Total	0.0054	0.0001	0.98
	Foliar	0.0030	0.0001	0.97

Intercept values were not significantly different than zero.

random and vascular plant species composition was determined on these plots just as it was done for the collars. All the biomass was clipped to the surface of the *Sphagnum*, sorted by species, separated into woody, foliar and fruiting parts, and then dried and weighed. Linear equations for the relationship between biomass and (stem number \times mean height) were determined for four groups: herbaceous plants, deciduous shrubs and trees, evergreen shrubs, and *Vaccinium oxycoccus* (Table 1). *Vaccinium oxycoccus* was not grouped as an evergreen shrub because of its structure; it is low-lying with small leaves, while *Chamaedaphne calyculata*, the dominant evergreen shrub, is a tall, woody plant. Foliar rather than total biomass usually formed a stronger relationship ($R^2 > 0.78$) to (stem number \times mean height) (Table 1).

The allometric equations developed from the clipped plots were used in conjunction with the (stem number \times mean height) for each of the 10 manual and 10 automated chambers to estimate total and foliar biomass. Two of the automated chambers in particular had characteristics that caused them to stand out from the others. Of all the chambers, a3 and a6 were the two with the highest total and foliar plant biomass (Table 2). By removing them from the analyses that did not take foliar biomass into account (all but comparison V), the automated and manual chambers were more comparable in terms of the range of biomass.

Environmental factors

The position of the water table relative to the peat surface for each chamber location was determined by measuring the height of the peat surface above the water table at the nearest well using a tube leveling device. This was repeated twice during the summer, in mid-July and mid-August. Chamber and air temperature were measured in the manual chambers in the LiCor 6200 sensor head (LiCor, Inc., Lincoln, NE). Type-T thermocouples (Omega Engineering, Stamford, CT) measured air and peat surface temperature in each automated chamber. The thermocouples in chamber a8 were malfunctioning during the

Table 2. Total and foliar biomass (g m^{-2}), and water table (cm, between the surface of the peat and the water table) of each automated and manual chamber. Both biomass and water table vary seasonally; biomass values were recorded in mid-July, 2000 and 2001, and water table was measured twice, in July and August, 2001 (mean reported).

	Biomass (g m^{-2})		Water table (cm)	Vascular species
	Total	Foliar		
<i>Auto.</i>				
a10	121	75	13.3	<i>Carex rostrata, Chamaedaphne calyculata</i>
a8	156	104	4.7	<i>Chamaedaphne calyculata</i>
a1	253	114	14.0	<i>Carex rostrata, Vaccinium oxycoccus</i>
a9	181	121	18.8	<i>Chamaedaphne calyculata, Carex rostrata, Vaccinium oxycoccus</i>
a5	239	155	10.1	<i>Chamaedaphne calyculata, Vaccinium oxycoccus</i>
a4	231	163	18.6	<i>Carex rostrata, Chamaedaphne calyculata, Vaccinium oxycoccus</i>
a2	300	201	17.5	<i>Vaccinium oxycoccus, Chamaedaphne calyculata, Carex rostrata</i>
a7	408	230	15.1	<i>Chamaedaphne calyculata</i>
a6	1007	427	20.4	<i>Alnus incana, Chamaedaphne calyculata</i>
a3	1004	488	20.6	<i>Chamaedaphne calyculata</i>
<i>Man.</i>				
m8	173	116	23.0	<i>Carex rostrata, Chamaedaphne calyculata</i>
m7	186	127	22.2	<i>Chamaedaphne calyculata, Carex rostrata</i>
m10	242	140	18.4	<i>Chamaedaphne calyculata</i>
m3	235	143	18.0	<i>Vaccinium oxycoccus</i>
m5	207	149	23.4	<i>Carex rostrata, Vaccinium oxycoccus, Chamaedaphne calyculata</i>
m1	362	180	5.5	<i>Chamaedaphne calyculata, Vaccinium oxycoccus</i>
m2	353	183	14.4	<i>Chamaedaphne calyculata</i>
m6	394	187	37.3	<i>Chamaedaphne calyculata</i>
m9	489	265	23.6	<i>Carex rostrata, Chamaedaphne calyculata</i>
m4	807	346	17.1	<i>Alnus incana</i>

Dominant vascular plants are listed for each collar/chamber. Rows are sorted from low to high foliar biomass.

growing season, and thus this chamber was not included in analyses III and V, which require temperature measurements. A PAR sensor (LiCor, Inc., Lincoln, NE) was attached to the manual chamber and recorded PAR at each collar during a sampling run, whereas for the automated chambers PAR was determined by taking the means recorded by a PAR sensor and a calibrated gallium arsenide phosphide photodiode (Hammamatsu, Bridgewater, NJ) located at stationary points within the automated chamber array.

Data analysis

NEE measured by the automated and manual chambers was compared five ways to account for the variability among the factors affecting NEE:

I. Direct NEE Comparison at fixed light levels. The aim of this comparison was to examine mean seasonal NEE for the automated and manual chambers using only PAR increments (PAR is a main driver for NEE), prior to more in-depth comparisons, in order to determine whether automated and manual NEE values were in the same range. Comparing manual fluxes, measured weekly, to automated fluxes, measured every 3 h in the same PAR range, also aids in determining the frequency of sampling needed to obtain an accurate carbon budget estimate. Manual and automated mean seasonal NEE values were calculated for each chamber, at four light levels: high PAR ($\text{PAR} > 1000 \mu\text{mol m}^{-2} \text{s}^{-1}$), mid PAR ($600 < \text{PAR} \leq 1000 \mu\text{mol m}^{-2} \text{s}^{-1}$), low PAR ($100 < \text{PAR} \leq 600 \mu\text{mol m}^{-2} \text{s}^{-1}$), and zero PAR ($\text{PAR} = 0 \mu\text{mol m}^{-2} \text{s}^{-1}$). We chose four PAR increments because analogous PAR levels were simulated using shrouds for the manual chambers. In order to compare the manual data to the automated data that did not use shrouds, we estimated the PAR ranges produced by each shroud. Also, we did not include $0 < \text{PAR} \leq 100$ in our comparison because of the lack of manual measurements made during this light increment; we measured manual NEE on the sunniest days to capture the full light range, and the shroud blocking 3/4 of the light resulted in only five PAR readings between 0 and 100 for the entire growing season, representing only three chamber sites.

Automated and manual chamber mean NEE values (n = number of chambers) were then compared using Wilcoxon rank-sum tests. The Wilcoxon rank-sum test is a nonparametric test used to compare variability between two groups of data to variability among each group. It differs from the t -test in that it does not assume that the data are normally distributed. Our data were not normally distributed because we installed each chamber in the fen in order to capture the range of vegetation.

II. NEE Comparison after temperature adjustment. Ambient temperature is a main driver of respiration, and automated and manual chamber respiration was measured under different temperature regimes. Manual respiration was estimated using shrouds in the middle of the day whereas automated respiration was measured during the nighttime, when PAR was naturally equal to zero, and temperatures were approximately 15 °C cooler than daytime temperatures. The aim of this comparison was to adjust for these temperature differences and then compare NEE at similar PAR levels. Adjusting manual respiration for the difference in temperature, involved several steps. First, the relationship between PAR and ambient temperature in the automated chambers was used to simulate the temperature that would have occurred naturally at the manual PAR values obtained with shrouds. The temperature adjustment was only computed for manual $\text{PAR} < 1000 \mu\text{mol m}^{-2} \text{s}^{-1}$ (because $\text{PAR} > 1000 \mu\text{mol m}^{-2} \text{s}^{-1}$ was measured under the same temperature regimes in both chamber systems for the most part) The adjustment was computed using the following equation:

$$\text{Air temperature} = 0.0124(\text{PAR}) + 14.997(R^2 = 0.61, \quad p < 0.001). \quad (1)$$

The air temperature recorded by the thermocouples inside the automated chambers tended to be slightly higher than the ambient air, especially at high PAR.

The second step was to determine $\ln(-\text{respiration})$ vs. temperature regression equations for each manual chamber (Eq. (2)). Then, the adjusted temperature for each manual value was inserted into the regression equation to determine the adjusted manual respiration value. Dawn and dusk were also significantly cooler than daytime, so the manual runs blocking half and three-quarters of the light required adjustment as well. In order to do this, photosynthesis and respiration were separated by subtracting the dark run (total respiration) from NEE at half and three-quarters PAR. The adjusted respiration values were then added to photosynthesis to obtain a final adjusted NEE value. These final adjusted NEE values were compared to automated NEE using the same method as the direct comparison.

In order to further validate the temperature adjustment, we measured nighttime NEE with the manual chambers on two occasions during the summer of 2001, and found it well within the range of automated nighttime NEE over the same temperature interval.

III. Comparison of respiration and temperature relationship. A log-transformed relationship was fit to the respiration and air temperature data:

$$\ln(-\text{respiration}) = \beta_0 * \text{temperature} + \beta_1. \quad (2)$$

Best-fit values for β_0 (slope) and β_1 (y-intercept) were found and Q_{10} values (increase in respiration for every 10 °C increase in temperature; another way to express slope) were calculated for each chamber individually. Wilcoxon rank-sum tests were performed using the individual chamber parameter fits (n = number of chambers) to compare the automated and manual values. Q_{10} responses have been calculated in a number of peatland studies using this relationship (e.g. Bubier et al. 1998, 2003a; Lafleur et al. 2003). Although other temperatures were investigated, air temperature (which is highly correlated with peat temperature at 5 cm depth) gave the strongest result.

IV. Comparison of NEE and PAR relationship, before and after temperature adjustment. A rectangular hyperbolic saturation curve, or Michaelis–Menten equation, was fit to the NEE and PAR data (e.g. Thornley and Johnson 1990; Froelking et al. 1998). The equation used to predict NEE using PAR was

$$\text{NEE} = \frac{(\text{GP}_{\text{max}} * \alpha * \text{PAR})}{(\text{GP}_{\text{max}} + \alpha * \text{PAR})} + \text{RSP}. \quad (3)$$

GP_{max} is maximum gross photosynthesis, which is the theoretical maximum rate of photosynthesis at infinite PAR. Mathematically it is the horizontal asymptote that signifies the upper bound of the data minus the respiration parameter. With unlimited light availability however, plants can become light saturated (usually at $\text{PAR} > 1000 \mu\text{mol m}^{-2} \text{s}^{-1}$) and factors such as leaf area, water or nutrient availability, or CO_2 supply become limiting. In the field, plants may not actually

reach their maximum photosynthetic capacity at maximum PAR. Photosynthesis can decrease under high PAR because high light can cause plants to become too hot and dry so their stomata close in order to conserve water or energy. The PAR level at which saturation is reached provides important theoretical information. The initial slope of the rectangular hyperbola, alpha (α), can be considered quantum efficiency, or how fast the plants respond to increasing PAR at low light levels. Respiration (RSP) is the y -intercept of the NEE vs. PAR curve, or NEE when PAR, and thus photosynthesis, is zero. The convention used in this paper is that positive NEE represents a net uptake of CO_2 by the ecosystem, whereas negative NEE represents net release of CO_2 to the atmosphere. Best-fit values for GP_{max} , α and RSP were found for each chamber individually, and Wilcoxon rank-sum tests were performed using the individual chamber parameter fits between the automated and manual values. Manual values were then adjusted for temperature, and the Wilcoxon rank-sum tests between the automated and manual values were re-calculated.

V. NEE comparison after consideration of environmental and biotic factors combined. The manual chambers were installed across the apparent trophic gradient, which also covered a broad range of vegetation communities. The automated chambers were installed with the goal of capturing the range of plant species present in order to obtain representative estimates of the overall carbon budget of the fen. NEE varied greatly among chambers of the same type (automated or manual) due to differences in species composition, biomass, and water table (Figure 3). Any environmental factor that has been shown to affect NEE, and that varies among replicates, will improve the comparison between chamber types if it is taken into account. Initially we attempted to compare chambers with similar characteristics, but when one characteristic was similar, another varied so that no clear pattern could be detected. Thus, we designed a nonlinear statistical model, based on published evidence of ecological patterns (Wieder 2001; Frohling et al. 2002; Bubier et al. 2003b), which includes PAR, temperature, foliar biomass, and water table in one equation.

The model was set up as the sum of two parts: an estimate of photosynthesis and an estimate of respiration. The photosynthesis component was based on the Michaelis–Menten relationship between NEE and PAR (Eq. (3)), with foliar biomass (fb) included as a factor affecting GP_{max} . Non-vascular plant biomass was not included as a variable in the model because of the roughly 100% cover of *Sphagnum* moss throughout the fen. The respiration component was based on the $\ln(-\text{respiration})$ vs. temperature (T) relationship. Relative water table depth (wt) was included in the denominator of the respiration component because water table and respiration are inversely related (Moore and Dalva 1993; Bubier et al. 2003b). Foliar vascular plant biomass was included, because it affects respiration as well as GP_{max} . NEE was not temperature adjusted because temperature and PAR were variables in the model. Significance tests indicated that none of the parameters could be eliminated from the model. The model is as follows:

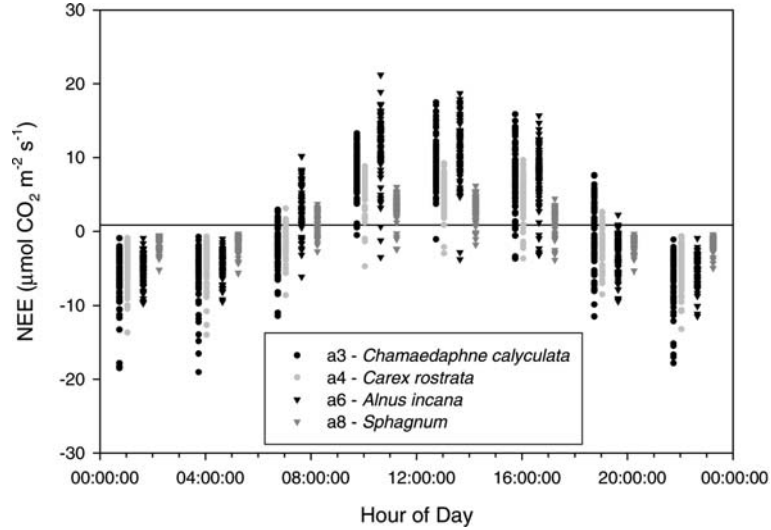


Figure 3. Automated NEE separated by chamber, with the dominant plant species assigned to the chambers vs. hour of the day. Each data point represents the NEE over one 2.5-min run, and each data series represents one chamber, the one with the highest biomass of the assigned species. Data include points from the entire growing season, showing variability in NEE based on differences in plant biomass and species composition.

$$NEE = \frac{\beta_1 * fb * \alpha * PAR}{(\beta_1 * fb) + \alpha * PAR} + \frac{\beta_3 * fb * e^{\beta_2 * T}}{wt}. \quad (4)$$

The parameter β_1 is related to GP_{max} from Eq. (3) in that $\beta_1 * fb = GP_{max}$. The parameter β_2 is associated with temperature, and β_3 is associated with fb/wt . Best-fit values, determined by least squares, for α and β_{1-3} were found for each chamber individually, and Wilcoxon rank-sum tests were performed using the individual chamber parameter fits, to compare the automated and manual values.

To determine quantitatively whether including chamber type would significantly improve the model, an F-test was performed comparing the model with and without chamber type as a variable. To do this, -1 was assigned to automated chambers and $+1$ to manual chambers. Then chamber type times a parameter was added to Eq. (4). This new equation was compared to Eq. (4) and the F-test was performed using data from all 19 chambers combined (chamber a8 could not be included due to the missing temperatures).

Results

I. Direct NEE comparison at fixed light levels. NEE recorded by the automated and manual chambers was in the same range; -10.8 to $12.7 \mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$ in the manual chambers and -17.2 to $13.1 \mu\text{mol}$

Table 3. Mean seasonal automated and manual NEE for high PAR and zero PAR (units of NEE are $\mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$).

Auto.	NEE	<i>n</i> size	Manual	NEE	<i>n</i> size	Temp. corr.
(a) PAR > 1000 $\mu\text{mol m}^{-2} \text{ s}^{-1}$						
a10	3.38 (0.11)	94	m8	5.47 (0.55)	14	
a8	3.59 (0.10)	102	m7	5.22 (0.37)	14	
a1	5.05 (0.18)	96	m10	4.96 (0.48)	17	
a9	4.50 (0.11)	102	m3	6.98 (0.66)	17	
a5	3.16 (0.12)	100	m5	7.39 (0.59)	17	
a4	5.88 (0.14)	121	m1	3.15 (0.68)	12	
a2	7.53 (0.20)	95	m2	4.45 (0.41)	24	
a7	2.85 (0.10)	98	m6	6.75 (0.70)	12	
			m9	5.01 (0.46)	14	
			m4	7.13 (0.60)	20	
(b) PAR = 0 $\mu\text{mol m}^{-2} \text{ s}^{-1}$						
a10	- 2.08 (0.08)	178	m8	- 3.86 (0.31)	14	- 1.04
a8	- 1.60 (0.07)	169	m7	- 5.08 (0.47)	14	- 0.66
a1	- 3.20 (0.13)	189	m10	- 4.31 (0.36)	14	- 0.71
a9	- 2.78 (0.10)	183	m3	- 7.51 (0.48)	13	- 1.87
a5	- 4.34 (0.25)	171	m5	- 4.52 (0.46)	12	- 0.60
a4	- 3.33 (0.19)	175	m1	- 6.40 (0.46)	11	- 1.43
a2	- 3.24 (0.13)	176	m2	- 4.91 (0.33)	14	- 0.74
a7	- 3.22 (0.15)	183	m6	- 6.03 (0.37)	14	- 3.50
			m9	- 5.12 (0.37)	14	- 0.94
			m4	- 8.10 (0.65)	13	- 1.30

Parts a and b show the mean, standard error (SE), and number of flux measurements (*n* size). Part b, also shows the mean manual NEE when PAR = 0, adjusted for temperature (Temp. corr.). This adjustment was done with the best-fit lines from $\ln(-1 * \text{resp.})$ vs. temperature analysis for each collar, and the mean nighttime air temperature recorded by the automated chambers (13.1 °C). Rows are sorted from low to high foliar biomass. Each mean is based on daily measurements; the SEs were computed assuming independence. Values in parentheses are standard errors.

Table 4. Comparison of NEE for the two chamber types, at four levels of PAR, with and without temperature correction.

	Direct comparison			Temp. corrected	
	<i>p</i> -value	Auto. mean	Man. mean	<i>p</i> -value	Man. mean
PAR > 1000	0.2031	4.49 (0.57)	5.65 (0.43)	NA	NA
600 < PAR ≤ 1000	0.8968	3.98 (0.78)	3.56 (0.47)	0.2743	4.64 (0.37)
100 < PAR ≤ 600	0.0031*	1.37 (0.40)	- 0.39 (0.26)	0.8286	1.54 (0.30)
PAR = 0	0.0002*	- 2.97 (0.30)	- 5.58 (0.44)	0.2370	- 2.41 (0.31)

The *p*-values are associated with Wilcoxon rank-sum tests that compare variability between chamber types to variability among chambers within types (*n* = number of chambers). Stars indicate that the chambers were significantly different at *p* < 0.05. Values in parentheses are standard errors.

$\text{CO}_2 \text{ m}^{-2} \text{ s}^{-1}$ in the automated chambers (Figure 2, Table 3). From May 24 to August 29, 2001, maximum NEE values followed the same trend in both types of chambers (Figure 2). However, there was a gradual increase in the

respiration recorded by the automated chambers, which may be attributed to the decrease in water table over the season. Mean seasonal respiration and NEE at low PAR were significantly more negative in the manual chambers than in the automated chambers, but NEE was not statistically different at $\text{PAR} > 600 \mu\text{mol m}^{-2} \text{s}^{-1}$ (Table 4).

II. NEE Comparison after temperature adjustment. NEE varies within each chamber type due to factors such as foliar biomass, species composition, or water table, and within an individual chamber due to factors such as PAR and temperature (Figure 3). These factors can be taken into account by incorporating them into equations, or adjusting values when there is a difference in methodology, such as the different temperature regimes associated with respiration. Manual respiration was greater when measured under a higher temperature regime, during the day, as opposed to the nighttime measurements recorded by the automated chambers (Figure 4). And thus, when NEE was adjusted for temperature in the manual chambers and compared at all four light levels, Wilcoxon rank-sum tests showed that there was no significant difference between automated and manual chambers (Table 4).

III. Comparison of respiration and temperature relationship. The p -values for slope, Q_{10} , and y -intercept of the respiration vs. temperature regression lines

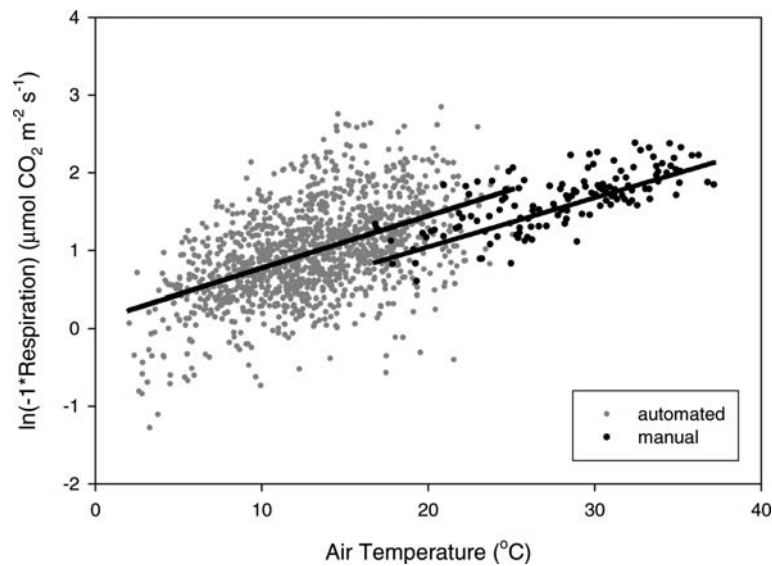


Figure 4. Natural log of respiration vs. air temperature ($^{\circ}\text{C}$) for the manual ($n = 133$) and automated ($n = 1280$) chambers. The different temperature range was due to automated respiration measured at night, and manual respiration measured under simulated dark conditions with shrouds during the day. Automated air temperature was measured by thermocouples in the chamber and manual air temperature was measured by thermocouples in the sensor head of the LI-6200. Each data point corresponds to one 2.5-min run. (auto. = $0.0673x + 0.0978$, $R^2 = 0.2435$, slope p -value = 0, y -int p -value = 0.0318, and man. = $0.0557x + 0.0843$, $R^2 = 0.5078$, slope p -value = 0, y -int p -value = 0.5372). See Table 5 for regression comparison.

Table 5. Comparison of fitted regressions of $\ln(\text{respiration})$ on temperature for the two chamber types.

	p -value	Auto. mean	Man. mean
Slope	0.0504	0.072 (0.006)	0.056 (0.005)
y -intercept	0.8125	0.045 (0.074)	0.089 (0.174)
Q_{10}	0.0553	2.072 (0.214)	1.765 (0.084)

A separate regression was run for each chamber; the Wilcoxon rank-sum tests compare variability between chamber types to variability among chambers within types. The p -values are associated with each Wilcoxon rank-sum test comparing the slope, Q_{10} , and y -intercept. Stars indicate that the chambers were significantly different at $p < 0.05$. Values in parentheses are standard errors.

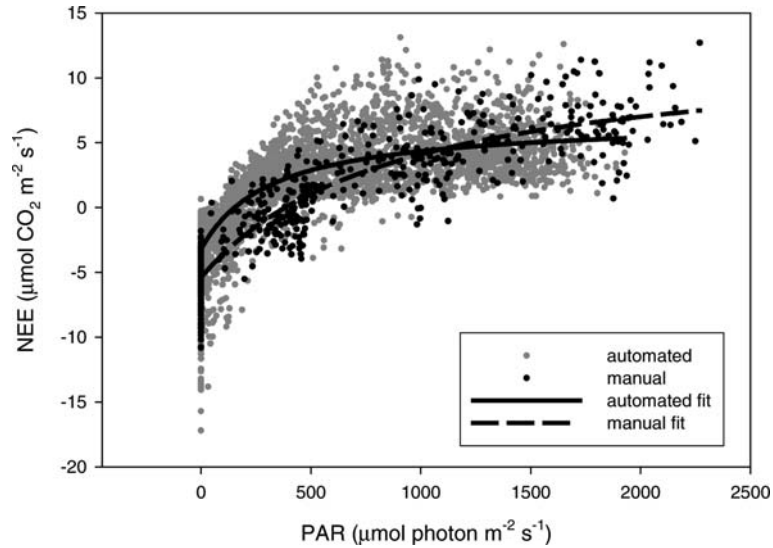


Figure 5. NEE vs. PAR over the entire growing season for manual ($n = 521$) and automated ($n = 5124$) chambers. Manual PAR range was created artificially by shrouding. Each data point corresponds to one 2.5-min run. See Table 6 for statistical comparisons.

were greater than 0.05 (Table 5). This indicates that automated and manual chamber fluxes fell on statistically indistinguishable regression lines (i.e. statistically the same slope and intercept) (Figure 4). Individual p -values for $\ln(-\text{respiration})$ vs. temperature lines were well below 0.05 for all manual and automated chambers, and R^2 values ranged from 0.61 to 0.86 in the manual chambers with one exception of 0.22, and from 0.11 to 0.59 in the automated chambers. These R^2 values would have been higher if the temperature range sampled was larger.

IV. Comparison of NEE and PAR relationship, before and after temperature adjustment. The quantum efficiency (α) was significantly lower in the manual than in the automated chambers, before and after temperature adjustment (Figures 5 and 6, Table 6). Adjusting for temperature in the manual chambers

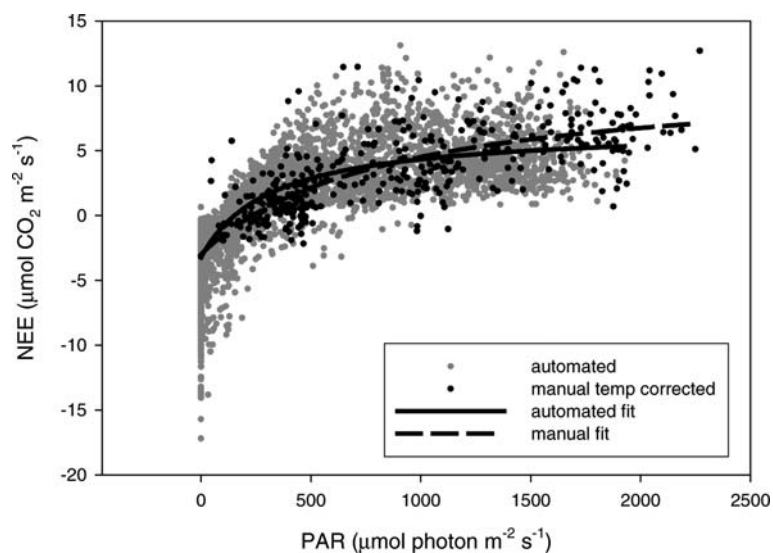


Figure 6. NEE vs. PAR over the entire growing season for manual ($n = 521$) and automated ($n = 5124$) chambers. Manual PAR range was created artificially by shrouding, and points with PAR under $1000 \mu\text{mol m}^{-2} \text{s}^{-1}$ were adjusted for temperature. Manual temperature was adjusted using the PAR vs. temperature relationship determined with the automated chamber data ($R^2 = 0.61$), and the new temperature was used to adjust the respiration using the respiration vs. temperature relationships. Each data point corresponds to one 2.5-min run. See Table 6 for statistical comparisons.

Table 6. Comparison of fitted Michaelis–Menten parameters for the two chamber types.

	Direct comparison			Temp. corrected	
	p -value	Auto. mean	Man. mean	p -value	Man. mean
α	0.0085*	0.0339 (0.0035)	0.0204 (0.0040)	0.0117*	0.0185 (0.0014)
GP_{max}	0.0003*	9.783 (1.0796)	18.224 (2.1320)	0.0062*	14.816 (0.6665)
RSP	0.0005*	- 3.283 (0.3409)	- 5.462 (0.4642)	0.2743	- 3.031 (0.1304)

A separate equation was fitted for each chamber; the Wilcoxon rank-sum tests compare variability between chamber types to variability among chambers within types. The p -values are associated with each Wilcoxon rank-sum test comparing the α , GP_{max} , and respiration, before and after temperature adjustment. Stars indicate that the chambers were significantly different at $p < 0.05$. Values in parentheses are standard errors.

lowered α . GP_{max} was significantly higher in the manual chambers. Although adjusting for temperature in the manual chambers lowered GP_{max} , it was still higher than the automated chamber GP_{max} . RSP was statistically the same between the automated and manual chambers after temperature adjustment.

V. NEE Comparison after consideration of environmental and biotic factors combined. A Wilcoxon rank-sum test between the automated and manual

Table 7. Comparison of fitted models using environmental variables (foliar biomass, temperature, water table) for the two chamber types (with automated chambers a3 and a6 included).

	p -value	Auto. mean	Man. mean	Mean t -value
α	0.0005*	0.0504 (0.0080)	0.0199 (0.0016)	10.94 (0.2885)
β_1	0.0535	0.0845 (0.0092)	0.1202 (0.0137)	18.61 (0.5547)
β_2	0.6532	0.0342 (0.0035)	0.0361 (0.0031)	7.53 (0.2319)
β_3	0.7802	-0.2152 (0.0205)	-0.2430 (0.0441)	-9.78 (0.3501)

A separate equation was fitted for each chamber; the Wilcoxon rank-sum tests compare variability between chamber types to variability among chambers within types. The p -values are associated with each Wilcoxon rank-sum test comparing α , β_1 , β_2 , and β_3 . See Eq. (4) in text. Stars indicate that the chambers were significantly different at $p < 0.05$. Values in parentheses are standard errors.

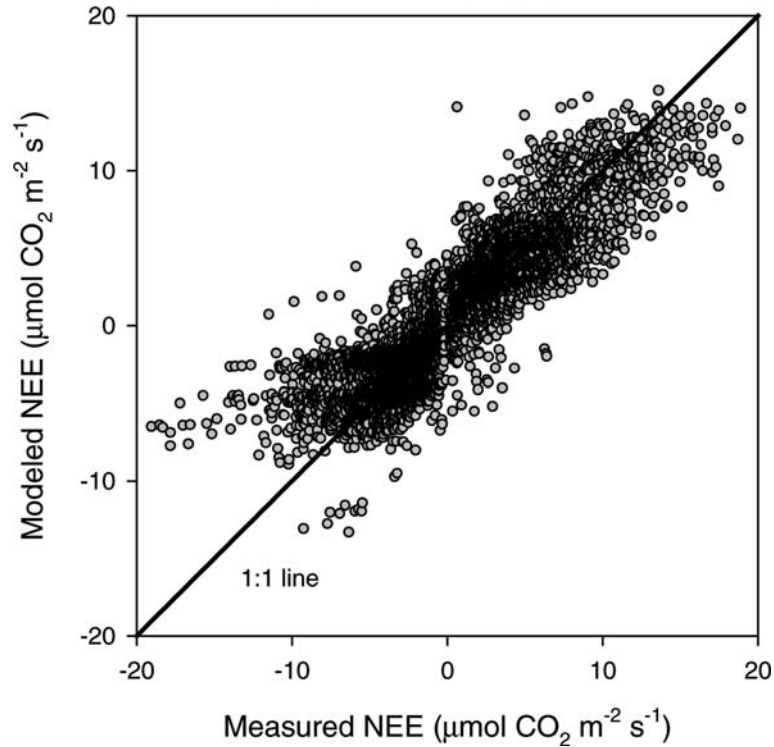


Figure 7. Predicted NEE vs. measured NEE of both automated and manual chambers using the best-fit model, Eq. (4) ($n = 6363$). Correlation coefficient is 0.89.

chamber best-fit parameters showed that parameters β_{1-3} were not statistically different, but that α was different (Table 7). Mean t -values associated with each parameter show that β_1 was the most significant, followed by α , β_3 , and then β_2 . Plotting measured NEE against the best-fit model above showed that the data

were clustered randomly along the 1:1 line (Figure 7). The correlation coefficient between measured and modeled NEE was 0.89. The model was most accurate when predicting NEE between -10 and $10 \mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$, which constituted 94.8% of the data.

An F-test indicated that the addition of chamber type as a variable did not significantly improve the fit of the model ($F = 2.10$, $p = 0.147$).

Discussion

I. Direct NEE Comparison at fixed light levels. The NEE values (ranging from -10.8 to $12.7 \mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$ in the manual chambers and -17.2 to $13.1 \mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$ in the automated chambers; Figure 2) are consistent with other studies of poor fens (Frolking et al. 1998). Savage and Davidson (2003) also found that weekly respiration measurements using manual chambers yielded the same seasonal fluxes as hourly automated data, and the manual chambers had smaller 95% confidence intervals. McGinn et al. (1998) put the manual chambers directly inside and outside of the automated chambers to sample the same area, as well as to test the chambers over the diurnal cycle. They found that the manual chambers measured consistently larger fluxes than the automated chambers. This may be a function of differences in chamber design. In our comparison the size and shape of the chambers and the sample gas flows were similar.

The NEE values at high PAR for both the automated and manual chambers could have been underestimated due to the assumption that CO_2 concentration decreased linearly throughout the 2.5-min runs, while in reality, it decreased less quickly at the end of a run because of plant stress. The automated data were rerun using 1.5-min runs (and only 3 means as opposed to 5) and the fluxes were approximately 5% higher. Our analysis also assumed that the flux was constant throughout a run, as do many static chamber studies.

II. NEE Comparison after temperature adjustment. Mean seasonal NEE at four light levels was not statistically different between the automated and manual chambers when adjusted for temperature. These results (Table 4) agree with Russell et al. (1998), who compared automated and manual chamber respiration from a boreal aspen forest. Scott et al. (1999) found that automated chambers gave higher cumulative values for gas exchange than the manual chambers, noting that the manual chambers missed many of the periods of high flux that the automated chambers were able to capture. In our data there were a few fluxes late in the season, both positive and negative, in which the automated chambers had higher values than any manual data (Figure 2). The number of these data was so few that they did not affect the mean NEE values enough to cause differences between the two systems. Manual sampling was done on one sunny day each week, so it is possible that the high automated fluxes were recorded on different, sunnier days and warmer nights. There was some overlap in temperature between the automated and manual respiration

data (Figure 4), which indicates that there did exist nighttime respiration values that were recorded at higher temperatures than some daytime values.

III. Comparison of respiration and temperature relationship. Our analyses determined that the automated and manual chamber respiration fluxes lie on the same $\ln(-\text{respiration})$ vs. temperature regression line (i.e. statistically the same slope and intercept), even though they were sampled at different temperature regimes. The p -values were just above 0.05 when comparing the slopes and Q_{10} values of the automated and manual chambers, which suggest that there may be some difference in how ecosystem respiration responds to increasing temperature during the day vs. at night. Or, plants could respond to increasing temperature slightly more efficiently at low temperatures, as suggested by the larger slope in the automated chambers, measured at cooler temperatures.

The mean slope of the $\ln(-\text{respiration})$ vs. temperature regression line, as well as mean respiration, was over twice what Bubier et al. (2003a) found for a mineral poor fen in Ontario, which was less productive, had smaller plant biomass, and was dominated by *Carex* species as opposed to evergreen and deciduous shrubs. More than three-quarters of the y -intercepts in this study were not significantly different than zero, suggesting that respiration approached $-1 \mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$ at freezing temperatures. Bubier et al. (2002) found that the largest efflux from the fen during winter months, $-3 \mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$, occurred at 0°C , but most of the fluxes ranged from 0 to $-1 \mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$. Possibly the $\ln(-\text{respiration})$ vs. temperature regression lines are more accurate within the observed ranges of temperature (approximately $5\text{--}25^\circ\text{C}$ for the automated chambers, and $20\text{--}38^\circ\text{C}$ for the manual chambers).

IV. Comparison of NEE and PAR relationship, before and after temperature adjustment. We found similar parameter estimates to Frolking et al. (1998) for the relationship between NEE and PAR in poor fens. Frolking et al. (1998) used manual chamber methods, and did not adjust for the differing chamber vapor pressure (Hooper et al. 2002) or temperature. Our manual chamber GP_{max} before Hooper et al. (2002) and temperature adjustments was $10.4 \pm 1.251 \mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$ compared to $11.5 \pm 0.4 \mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$ in Frolking et al. (1998); our α was $0.022 \pm 0.007 \mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1} / \mu\text{mol photons m}^{-2} \text{ s}^{-1}$ compared to $0.024 \pm 0.002 \mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1} / \mu\text{mol photon m}^{-2} \text{ s}^{-1}$; and our mean respiration was $-2.87 \pm 0.42 \mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$ compared to $-2.57 \pm 0.13 \mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$. After correcting for vapor pressure and temperature, our manual chamber GP_{max} , α , and mean respiration values in this study were $14.8 \pm 0.667 \mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$, $0.019 \pm 0.001 \mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1} / \mu\text{mol photon m}^{-2} \text{ s}^{-1}$, and $-3.03 \pm 0.13 \mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$ respectively (Table 6).

The automated and manual chamber NEE vs. PAR relationships had statistically the same respiration values when manual chamber values were adjusted for temperature. However, manual chamber α was significantly smaller than automated chamber α (Table 6). This is perhaps one of the most

important differences between the two measurement systems. The higher quantum efficiency in the automated chambers could be due to the lack of low PAR values recorded with the manual chambers; PAR between 0 and $200 \mu\text{mol m}^{-2} \text{s}^{-1}$ was rarely measured with the manual chambers because NEE was measured on sunny days with high PAR (on some days above $2000 \mu\text{mol m}^{-2} \text{s}^{-1}$), so the shroud blocking 3/4 of the light could still have PAR over $500 \mu\text{mol m}^{-2} \text{s}^{-1}$. Conversely, the automated α value was probably conservative due to the filtering of zero fluxes. Perhaps another reason for the difference in α is a temperature effect on photosynthesis, not solely respiration; low PAR for the manual chambers was simulated with shrouds and therefore was measured under higher temperatures than naturally low PAR times of day, which may alter photosynthesis. Temperature adjustment in the manual chambers changed the shape of the curve, which suggests that calculating parameters without this adjustment produces artificially high GP_{max} , and larger RSP (Table 6). However, temperature adjustment made the differences between manual and automated chamber α even more pronounced.

Manual GP_{max} was significantly larger than automated chamber GP_{max} even after temperature adjustment, which lowered the value (Table 6). This could be due to the ability to screen and repeat runs in the field when measuring NEE manually. In order to obtain more accurate NEE values, the run was repeated if the five means recorded by the LiCor 6200 decreased a large amount over the 2.5-min run. Automated chambers did not have the ability to do this, and thus if the means in a run dropped off due to plant stress inhibiting photosynthesis, the flux protocol would average the data, resulting in a lower NEE value.

V. NEE Comparison after consideration of environmental and biotic factors combined. We used nonlinear regression in this study to account for spatial heterogeneity, thus providing a more direct relationship between the automated and manual chambers. The photosynthesis component of the equation differed from the Thornley and Johnson (1990) equation used in the previous section, in that the GP_{max} parameter was replaced with foliar biomass times a parameter (β_1). The β_1 parameter was not significantly different between the automated and manual chambers (Table 7), which suggests that differences in foliar biomass caused the difference in GP_{max} . The α parameter was significantly larger in the automated chambers, which is consistent with the analysis in the previous section. β_2 and β_3 , the parameters associated with respiration, were not statistically different, indicating that when biomass and water table are taken into account, reducing some causes of variability in NEE, the chamber types are still comparable. (Frolking et al. 2002) included sapwood volume in the respiration component of their Peatland Carbon Simulator (PCARS). Bubier et al. (2003b) used stepwise linear regression to predict respiration with water table and temperature.

Plotting measured NEE against the best-fit model above showed some deviation from the 1:1 line at low and high NEE, which suggests that there is some factor that has not been taken into account. The purpose of this model was to include environmental and biotic factors that were variable among

individual chambers, in order to provide a more direct comparison between automated and manual chamber NEE.

An F-test comparing the model with and without chamber type as a variable indicated that including chamber type does not significantly improve the model. Therefore, differences in chamber type are not significant enough to affect the model. This is an encouraging result for showing the comparability of the two measurement systems.

Conclusions

Results of the five comparisons showed that NEE measurements made by the manual and automated chambers were in the same range. When sorted into four light regimes and adjusted for temperature differences, automated and manual chamber NEE and respiration were not significantly different. But differences were found in the NEE vs. PAR relationship with manual chambers providing higher maximum gross photosynthesis estimates (GP_{max}), and slower uptake of CO_2 at low light (α) even after temperature adjustment. Automated and manual chambers are both reliable techniques for measuring CO_2 exchange. There are several differences in the design of the systems that would cause one system to be more desirable than the other depending on the goals of the study and logistics. For example, if one wanted to study the quantum efficiency of plants in wetlands, using automated chambers would provide values with higher resolution, at nighttime temperature, and under naturally varying light conditions as opposed to shrouds used for manual measurements. However, studying maximum gross photosynthesis may be more accurate using the manual system, which allows for immediate surveillance and measurement repetition if necessary. Studying spatial variation in a wetland would be more feasible with the manual system, while the automated system would provide more information about temporal variability. Many interacting variables contribute to NEE, including PAR, temperature, water table, plant biomass, and species composition. Variations in any one of the contributing factors may cause significant variation in NEE. Our modeling analysis found that chamber type did not contribute to differences in NEE between the two measurement systems.

Automated chambers would probably provide a more accurate estimate of the growing season CO_2 flux in a single collar and in small wetlands, but without the ability to sample the spatial variation in large heterogeneous wetlands, automated chambers may not be as desirable as manual chambers for determining the ecosystem CO_2 balance even with the interpolations that must be performed to fill in gaps in the less frequent manual data. Further investigations using these data could include determining the adequate frequency of sampling to obtain an accurate carbon budget for the fen, sensitivity analysis of the model used in this study, and scaling up from individual chamber flux measurements to the annual carbon dioxide balance of the entire wetland.

Acknowledgements

Funding for this research was provided by a Cascade Mentoring Fellowship through Mount Holyoke College to EHB, a grant from NASA's New Investigator Program in Earth Science to JLB, and NASA Terrestrial Ecology Program grants to PMC. This research would not have been possible without the field, laboratory, and editorial assistance of Steve Frohking, Ed Rastetter, Aaron Ellison, Maria Hunter, Bianca Moebius, Ruth Varner, Al Werner, and Peter Czepiel. Jack Dibb, Nicola Blake, Sallie Whitlow, and Jeff Foggman kindly allowed our work at Sallie's Fen.

References

- Alm J., Schulman L., Walden J., Nykanen H., Martikainen P.J. and Silvola J. 1999. Carbon balance of a boreal bog during a year with an exceptionally dry summer. *Ecology* 80: 161–174.
- Ambus P. and Robertson G.P. 1998. Automated near-continuous measurement of carbon dioxide and nitrous oxide fluxes from soil. *Soil Sci. Soc. Am. J.* 62: 394–400.
- Aurela M., Laurila T. and Tuovinen J.-P. 2001. Seasonal CO₂ balances of a subarctic mire. *J. Geophys. Res.* 106: 1623–1637.
- Barford C.C., Wofsy S.C. and Goulden M.L., et al. 2001. Factors controlling long- and short-term sequestration of atmospheric CO₂ in a mid-latitude forest. *Science* 294: 1688–1691.
- Brown D.A. 1998. Gas production from an ombrotrophic bog – effect of climate change on microbial ecology. *Climate Change* 40: 277–284.
- Bubier J.L., Crill P.M., Moore T.R., Savage K. and Varner R.K. 1998. Seasonal patterns and controls on net ecosystem CO₂ exchange in a boreal peatland complex. *Global Biogeochem. Cycles* 12: 703–714.
- Bubier J.L., Crill P.M. and Mosedale A. 2002. Net ecosystem exchange of CO₂ measured by autochambers during the snow-covered season at a temperate peatland. *Hydrol. Process.* 16: 3667–3682.
- Bubier J.L., Bhatia G., Moore T.R., Roulet N.T. and Lafleur P.M. 2003a. Spatial and temporal variability in growing season net ecosystem carbon dioxide exchange at a large peatland in Ontario, Canada. *Ecosystems* 6: 353–367.
- Bubier J.L., Crill P.M., Mosedale A., Frohking S. and Linder E. 2003b. Peatland responses to varying interannual moisture conditions as measured by automatic CO₂ chambers. *Global Biogeochem. Cycles* 17(2): 1066, doi:10.1029/2002GB001946.
- Bubier J.L., Frohking S., Crill P.M. and Linder E. 1999. Net ecosystem productivity and its uncertainty in a diverse boreal peatland. *J. Geograph. Res.* 104: 27.
- Carroll P. and Crill P.M. 1997. Carbon balance of a temperate poor fen. *Global Biogeochem. Cycles* 11: 349–356.
- Conen F. and Smith K.A. 2000. An explanation of linear increases in gas concentration under closed chambers used to measure gas exchange between soil and the atmosphere. *Eur. J. Soil Sci.* 51: 111–117.
- Crill P.M., Keller M., Weitz A., Grauel B. and Veldkamp E. 2000. Intensive field measurements of nitrous oxide emissions from a tropical agricultural soil. *Global Biogeochem. Cycles* 14: 85–96.
- Davidson E.A., Savage K., Verchot L.V. and Navarro R. 2002. Minimizing artifacts and biases in chamber-based measurements of soil respiration. *Agric. Forest Meteorol.* 113: 21–37.
- De Villiers M. 2000. *Water: The Fate of Our Most Precious Resource*. Houghton Mifflin Company, Boston, MA, USA (Chapter 4).

- Frolking S., Roulet N.T., Moore T.R., Lafleur P.M., Bubier J.L. and Crill P.M. 2002. Modeling seasonal to annual carbon balance of Mer Bleue Bog, Ontario, Canada. *Global Biogeochem. Cycles* 16(3), doi: 10.1029/2001GB001457.
- Frolking S.E., Bubier J.L. and Moore T.R., et al. 1998. Relationship between ecosystem productivity and photosynthetically active radiation for northern peatlands. *Global Biogeochem. Cycles* 12: 115–126.
- Frolking S. and Crill P.M. 1994. Climate controls on temporal variability of CH₄ flux from a poor fen in southeastern New Hampshire; measurement and modeling. *Global Biogeochem. Cycles* 8: 385–397.
- Goulden M.L. and Crill P.M. 1997. Automated measurements of CO₂ exchange at the moss surface of a black spruce forest. *Tree Physiol.* 17: 537–542.
- Gregory J.M., Mitchell J.F.B. and Brady A.J. 1997. Summer drought in northern mid-latitudes in a time-dependent CO₂ climate experiment. *J. Climate* 10: 662–686.
- Hobbie S.E. 1996. Temperature and plant species control over litter decomposition in Alaska tundra. *Ecol. Monogr.* 66: 503–522.
- Hooper D.U., Cardon Z.G., Chapin F.S. and Durant M. 2002. Corrected calculations for soil and ecosystem measurements of CO₂ flux using the LI-COR 6200 portable photosynthesis system. *Oecologia* 132: 1–11.
- Joiner D.W., Lafleur P.M., McCaughey J.H. and Bartlett P.A. 1999. Interannual variability in carbon dioxide exchanges at a boreal wetland in the BOREAS northern study area. *J. Geophys. Res.* 104: 27663–27672.
- King J.A. and Harrison R. 2002. Measuring soil respiration in the field: an automated closed chamber system compared with portable IRGA and alkali absorption methods. *Commun. Soil Sci. Plant Anal.* 33: 403–423.
- Lafleur P.M., Roulet N.T., Bubier J.L., Frolking S. and Moore T.R. 2003. Interannual variability in the peatland-atmosphere carbon dioxide exchange at an ombrotrophic bog. *Global Biogeochem. Cycles* 17(2): 1036.
- Lafleur P.M., Griffiths T.J. and Rouse W.R. 2001. Interannual variability in net ecosystem CO₂ exchange at the arctic treeline. *Arctic, Antarctic, Alpine Res.* 33: 149–157.
- Laine J. and Minkkinen K. 1996. Effect of forest drainage on the carbon balance of a mire: a case study. *Scand. J. Forest Res.* 11: 307–312.
- McGinn S.M., Akinremi O.O., McLean H.D.J. and Ellert B. 1998. An automated chamber system for measuring soil respiration. *Can. J. Soil Sci.* 78: 573–579.
- Melloh R.A. and Crill P.M. 1996. Winter methane dynamics in a temperate peatland. *Global Biogeochem. Cycles* 10(2): 247–254.
- Moore T.R. and Dalva M. 1993. Influence of temperature and water table position on carbon dioxide and methane emissions from columns of peatland soils. *J. Soil Sci.* 44: 651–664.
- Oechel W.C., Hastings S.J., Vourlitis G., Jenkins R.M., Riechers G. and Grulke N. 1993. Recent change of arctic tundra ecosystems from a net carbon dioxide sink to a source. *Nature* 361: 520–523.
- Pumpanen J., Iivesniemi H., Keronen P., Nissinen A., Pohja T., Vesal T. and Hari P. 2001. An open chamber system for measuring soil surface CO₂ efflux: analysis of error sources related to the chamber system. *J. Geophys. Res.* 106: 7985–7992.
- Russell C.A., Voroney R.P., Black T.A., Blanken P.D. and Yang P.C. 1998. Carbon dioxide efflux from the floor of a boreal aspen forest. II. Evaluation of methods – verification by infra-red analysis of a dynamic closed chamber. *Can. J. Soil Sci.* 78: 311–316.
- Savage K.E. and Davidson E.A. 2003. A comparison of manual and automated systems for soil CO₂ flux measurements: tradeoffs between spatial and temporal resolution. *J. Exp. Bot.* 54: 891–899.
- Scott A., Crichton I. and Ball B.C. 1999. Long-term monitoring of soil gas fluxes with closed chambers using automated and manual systems. *J. Environ. Qual.* 28: 1637–1643.
- Shurpali N.J., Verma S.B., Kim J. and Arkebauer T.J. 1995. Carbon dioxide exchange in a peatland ecosystem. *J. Geophys. Res.* 100: 14319–14326.

- Thornley J.H.M. and Johnson I.R. 1990. *Plant and Crop Modelling: A Mathematical Approach to Plant and Crop Physiology*. Clarendon, Oxford, England.
- Vourlitis G.L. and Oechel W.C. 1999. Eddy covariance measurements of CO₂ and energy fluxes of an Alaskan tussock tundra ecosystem. *Ecology* 80: 686–701.
- Waddington J.M., Griffis T.J. and Rouse W.R. 1998. Northern Canadian wetlands: net ecosystem CO₂ exchange and climate change. *Climatic Change* 40: 267–275.
- Whiting G.J., Chanton J.P., Bartlett D. and Happell J. 1991. Relationships between CH₄ emission, biomass, and CO₂ exchange in a subtropical grassland. *J. Geophys. Res.* 96: 13067–13071.
- Wieder R.K. 2001. Past, present, and future peatland carbon balance: an empirical model based on ²¹⁰Pb-dated cores. *Ecol. Appl.* 11: 327–342.